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CONDITIONS FOR SPONTANEOUS FORMATION OF HIGHLY DISPERSED, CONCENTRATED EMULSIONS

I. DEPENDENCE OF THE DEGREE OF DISPERSION OF EMULSIONS ON THE MOLECULAR NATURE OF THE EMULSIFIERS

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The spontaneous emulsification effect consists of the formation of emulsions without any external action causing dispersion of the liquid, with a sharp decrease of surface tension at the separation boundary of the two liquid phases down to tenths and hundredths of one erg/cm². Emulsions are spontaneously formed on dilution, with water, of homogeneous mixtures (solubilized solutions) of water, a hydrocarbon, and diphilic substances, that is, polar substances which have an affinity simultaneously both for water and the hydrocarbon-emulsifiers of the soap type and of the type of molecularly soluble surface active compounds: alcohols, organic acids, amines, etc. [1]. Such mixtures are usually concentrated with respect to the hydrocarbon and the emulsifier. This method of emulsification is widely used in technology for the preparation of coolant lubricants used for the treatment of metals by cutting and pressure, by the dilution of mixtures known as emulsols [2]. Emulsols consist of mineral oil, a small amount of water, sometimes alcohol, and emulsifiers. High grade emulsols should have good emulsifiability, i.e., should give highly dispersed, stable, and concentrated emulsions. The emulsifiability of an emulsol is closely related to the nature of its component ingredients. Study of this relationship is of great importance for the physico-chemical basis of formulations and properties of emulsols, and at the same time it has an undoubted theoretical interest.

The aim of the present work was to study the dependence between the emulsifying power of substances in the spontaneous emulsification process and their molecular nature -- their hydro- or oleophilic nature in the sense of an affinity for water or hydrocarbons. With this aim, the degree of dispersion of emulsions obtained with the same oil but with different emulsifiers was examined in relation to the surface activity of the emulsifiers at the aqueous solution-air boundary of separation. The surface activity was taken as a relative measure of the hydro- or oleophily, on the general basis that the more hydrophobic a substance is, the greater is its surface activity in an aqueous medium.

EXPERIMENTAL, AND DISCUSSION OF RESULTS

The method of microscopical analysis was used to study the degree of dispersion of spontaneous emulsions of solar oil made with ammonium oleate, soda naphthenic soap, sodium butylnaphthalene sulfonate (Nekal), and with the mixtures: oleum. oleate + Nekal, ammonium oleate + Petrov kontakt soda soap (sodium sulfonaphthenate). Soaps of oleic and naphthenic acids, and neutralized Petrov kontakt are usual components of emulsols; sodium butylnaphthalene sulfonate was tested by us as a possible soap substitute for emulsols. These substances are representative of four different classes of emulsifiers: fatty acid soaps, naphthenic soaps, sulfonaphthenic acid soaps, and synthetic detergents of the sulfonate class. For preparation of the emulsols, the soap, used in the form of a 60-80% product, was mixed with the oil by heating on the water bath.

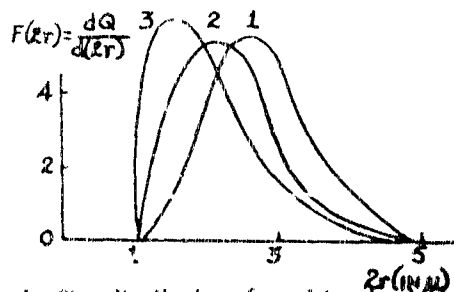


Fig. 1. Size distribution of emulsion droplets:
1) 50% solar oil + 50% sodium butylnaphthalene sulfonate; 2) the same + 50% ammonium oleate; 3) the same + 50% naphthenic soap.

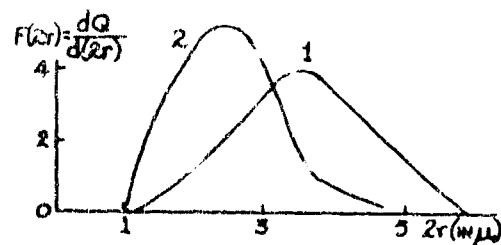


Fig. 2. Size distribution of emulsion droplets: 1) 60% solar oil + 40% ammonium oleate; 2) the same + 40% naphthenic soap.

Evaluation of the hydro- or oleophily by the surface activity was examined in detail in another paper, together with surface tension isotherms. From the surface tension measurements, the emulsifiers may be arranged in the following series of increasing hydrophily: ammonium oleate < naphthene soap < Petrov kontakt soap < sodium butylnaphthalene sulfonate.

The distribution curve for droplet size for emulsions formed from emulsols having the ratio oil: soap (anhydrous) 1:1, show that both the relatively hydrophobic oleate and also hydrophilic Nekal give more coarsely dispersed emulsions than naphthene soap, which occupies an intermediate position in the hydrophily order (Fig. 1). If the emulsol contains 60% oil, oleate gives a relatively coarsely dispersed emulsion, naphthene soap a finer one, while in the case of Nekal part of the oil is not emulsified at all but separates out in a layer immediately on dilution of the emulsol (Fig. 2).

Figs. 3 and 4 compare the emulsifying power of ammonium oleate and mixture of ammonium oleate with Nekal. The emulsifying power of a mixture of emulsifiers is greater than that of each one separately. The degree of dispersion of the emulsions increases with increase of the relative content of Nekal, although Nekal itself is inferior to ammonium oleate as an emulsifier.

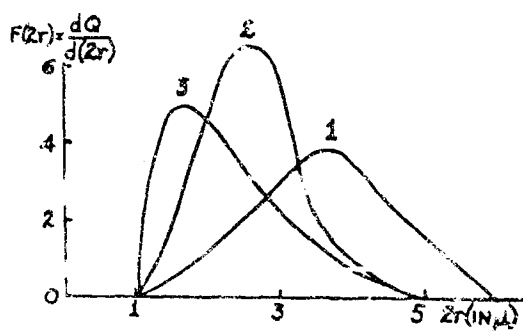


Fig. 3. Size distribution of emulsion droplets: 1) 60% solar oil + 40% ammonium oleate; 2) the same + 30% ammonium oleate + 10% Nekal; 3) the same + 10% ammonium oleate + 30% Nekal.

ing to Trapezhnikov's data, corresponds to an adsorptional layer which is close to saturation, after which the stabilizing effect decreases sharply with increasing saturation. Thus, the colloidization of the emulsifier in the surface layer should not be maximum, but it has a certain optimum value at which the stabilizing film combines adequate structural strength with the power of quickly repairing occasional damage. On the basis of these views, substances with some average degree of hydro- or oleophily should be the best stabilizers. Strongly hydrophobic emulsifiers have high surface activity in an aqueous medium, but the adsorptional envelopes which they form will not hydrate readily and, as the result of extensive colloidization of the protective film, brittle fractures may arise in it. Strongly hydrophilic emulsifiers, on the other hand, will give rise to adsorptional layers which are mobile and well-hydrated, but are not sufficiently structurized, and in addition, the initial degree of dispersion of the emulsion may be low because of the weak surface activity of the emulsifier. The combination of requirements in stabilizers is provided by "balanced emulsifiers" in which the polar and non-polar parts of the molecules are developed sufficiently and to approximately equal extents. These are emulsifiers of medium hydro- or oleophily, and therefore of medium surface activity.

Evidently, in our experiments the mixture, with respect to the hydrophilic and hydrophobic emulsifiers — oleate and Nekal — is equivalent to a "balanced emulsifier". When the mixture is used, a mixed adsorption-solvational

Even when the emulsol prepared with oleate only contains much less oil (50%) than the emulsol with a mixed emulsifier (70%), the degree of dispersion formed by the latter is found to be somewhat higher (Fig. 5). Similar results were also obtained for a mixture of ammonium oleate with Petrov kontakt soap: the mixture emulsifies oil better than does oleate (Fig. 6). The degree of dispersion of the emulsion decreases with increasing concentration of solar oil from 60 to 70% in the emulsol.

We propose the following possible explanation of the results obtained. For a substance to be a good emulsifier it should have high surface activity at the oil/water boundary of separation, and a power of forming an adsorption-solvational envelope around the oil droplets, which hinders their coalescence on collision. As was shown in a number of papers by Rehinder and his coworkers [3], such an envelope should have high structural viscosity or strength, should be readily hydrated (in the case of an o/w emulsion) and should repair itself easily, or restore its structure at local points of breakage. The maximum stabilizing action, according

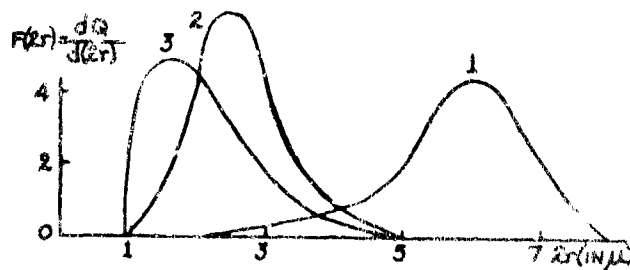


Fig. 4. Size distribution of emulsion droplets: 1) 70% solar oil + 30% ammonium oleate; 2) the same + 20% ammonium oleate + 10% Nekal; 3) the same + 10% ammonium oleate + 20% Nekal.

film is formed around the emulsion droplets. The more oleophilic component (oleate) confers adequate structural strength to this film, while the more hydrophilic component (Nekal) gives it the power of self-repairing and good capacity for being hydrated. Naphthenic soap, which occupies an intermediate position between oleate and Nekal in surface activity, evidently has the optimum ratio of polar to nonpolar groups which is essentially necessary for good stabilizing action. It is, therefore, an effective emulsifier and is superior to oleate and Nekal.

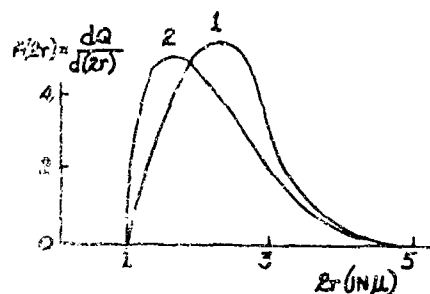


Fig. 5. Size distribution of emulsion droplets: 1) 50% solar oil + 50% ammonium oleate; 2) 70% solar oil + 10% ammonium oleate + 20% Nekal.

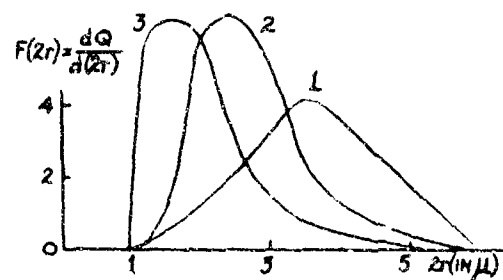


Fig. 6. Size distribution of emulsion droplets: 1) 60% solar oil + 40% ammonium oleate; 2) the same + 30% ammonium oleate + 10% Petrov kontakt soap; 3) the same + 10% ammonium oleate + 30% Petrov kontakt soap.

All that has been said above concerning the dependence between the stabilizing effect and the hydro- or oleophilicity of the emulsifier applies both to emulsions obtained by mechanical dispersion, and to spontaneously formed emulsions, and in case of the latter, independently of the method of their formation or the mechanism of the process, because, whatever the course of this process, its final result is a system which obeys the general laws for disperse systems. The literature contains indications of the high emulsifying powers of emulsifier mixtures in the production of emulsions by the usual mechanical method [4]. A similar effect was also found by Rashkovan for a mixture of soap and alcohol [5]. The degree of dispersion of emulsions obtained with such combined emulsifiers is higher than if soap only is used. The author's explanation for this is that the alcohol, by virtue of its high surface activity, favors an increase of the initial degree of dispersion of the emulsion, and the highly dispersed emulsion formed will be more stable, because the alcohol, which dissolves molecularly, "dilutes" the adsorptional envelope and ensures that it remains intact.

At the present time it is still impossible to determine the role of emulsifiers in spontaneous emulsification completely and precisely, as the mechanism of this effect has not been elucidated with certainty. In addition to a sharp lowering of the interphase surface tension, which is required for the spontaneous formation of a highly dispersed emulsion and for a stabilizing effect, the following functions of the emulsifier may also be noted: 1) it assists the mixing of large amounts of oil and water, and so makes possible the formation of an emulsol; 2) it determines the nature of the continuous phase of the emulsol; 3) it determines the peptizability of the system which, according to the views given below on the mechanism of spontaneous formation of emulsions, plays a significant part in this process. These factors are also closely related to the molecular nature of the emulsifier.

Our explanation of spontaneous emulsification is based primarily on the experimentally proved dependence between the degree of dispersion of the emulsifier in the solution and its solubilizing power. In the work of Yurzhenko and Kucher [7], Voyutsky and Perehudova [6], and others [8] it is established that the solubilizing power (the maximum amount of substance which can be absorbed by a given emulsifier solution) increases with the colloidal nature of the solution, i.e., with increase of the relative content of the colloiddally dispersed portion and of the micelle size. In accordance with this direct dependence between the colloidal nature of the solution and its solubilizing power, in the case of nonpolar hydrocarbons the specific solubilization (in Yurzhenko's terminology), or the solubilization calculated per 1 g emulsifier, is usually higher in concentrated, more highly colloidal solutions than in dilute solutions [6, 8, 9]. Evidently, the degree of colloidization of the emulsifier in the sols formed by dilution of emulsols is not sufficient to retain in solution all the oil contained in the emulsol. As a result, there is a certain excess of oil, which separates out of solution. Because of the presence of the emulsifier, the aggregation of the hydrocarbon molecules does not continue as far as the formation of a continuous phase, but ceases at the formation of droplets of a definite size, the further coalescence of which is prevented, as in mechanical emulsification, by the protective adsorptional layer formed on them. McBain [10], in his study of another type of spontaneous emulsification—in two-layer systems—noted that soap does not act as an emulsifier, and does not itself cause the formation of droplets, but serves as a stabilizer for droplets "that have been formed by some other means".

This occurs in our systems by the association of the hydrocarbon from a state of molecular or colloid dispersion, as the result of formation of a new system supersaturated with respect to oil, on dilution of the emulsol.

We therefore consider spontaneous emulsification as a condensation process caused by a decrease of the specific solubilization of the oil when the emulsol is diluted with water.*

The greater is the excess of oil at a given dilution, which corresponds to a higher oil : soap ratio, the more highly concentrated and coarsely dispersed will the emulsion formed be (Fig. 7). The higher is the concentrational

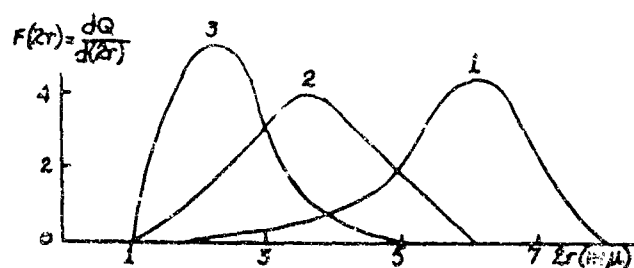


Fig. 7. Size distribution of emulsion droplets: 1) 70% solar oil + 30% ammonium oleate; 2) 60% solar oil + 40% ammonium oleate; 3) 50% solar oil + 50% ammonium oleate.

coefficient of the specific solubilization, i.e., the greater is the increase of the latter per unit increase of concentration, the more probable is the formation of an emulsion of microscopic particle size, since the greater will be the excess of oil on dilution.** If the value of the specific solubilization is constant, spontaneous emulsion formation should not take place. In Rebinder's laboratory [9] it was established that soap gels containing solubilized organic liquids spontaneously form emulsions on dilution, while in solutions this does not occur. In the light of the views put forward, this fact may be explained by the high concentration coefficient of the specific solubilization in the initial regions of the gels, with a sharp jump at the sol-gel transition point; for sols this coefficient is zero in the cases studied.

In order that an emulsion should be concentrated and that, as far as possible, the greater part of the added oil should form a highly dispersed emulsified phase, the emulsol should contain a large amount of oil and at the same time should be readily peptized by water. The solubilizing power of soap for hydrocarbons increases with its "hydrophobization", for example, with increase in the length of the nonpolar chain [8, 9, 12]. We found (see [13]) that the amount of oil which can be solubilized is greater as the maximum surface activity of the soap in aqueous solution is higher, i.e., as the soap is more hydrophobic. In accordance with this experimental result, the first condition — a high concentration of oil in the emulsol — may be fulfilled with a sufficiently hydrophobic emulsifier. The second condition requires more hydrophilic properties in the system. Consequently, in this respect also the best results may be given by an emulsifier of medium hydro- or oleophily, such as the naphtenic soap studied by us, or a mixture of two emulsifiers, one of which, the more hydrophobic (oleate) ensures the absorption of a sufficient amount of oil, and the other, the more hydrophilic (Nekal) confers better peptizability to the emulsol.

The above concepts and experimental data lead to the conclusion that for the preparation of a highly dispersed and stable concentrated emulsion, with a minimum "loss" of oil in a solubilized state in the dispersion medium, an emulsol should be used containing: 1) two emulsifiers, one of which is fairly hydrophobic, as shown by its high surface activity in aqueous solution, and the other is fairly hydrophilic (i.e., considerably less surface-active), or 2) one emulsifier of an intermediate character, i.e., with a more clearly defined diphilic character and medium surface activity. An explanation of the role of emulsifiers in the spontaneous emulsification process and a conclusion concerning the choice of emulsol composition was given by the present author in 1940 in P. A. Rebinder's laboratory.

* Increase of the specific solubilization with concentration may be the consequence not only of colloidization of the soap solution, but of other changes in the system. In some papers (those of Vojutsky [6, 11] and Lawrence [12]) there are indications that this increase may be due to change of the micelle shape — an increase of the relative content of plate-like micelles, which are more accessible than are spherical ones to penetration by hydrocarbons, and to a decrease in their degree of hydration. However, the significance of these two factors is not known with such certainty as the dependence of the solubilizing power of soap on its degree of association. We, therefore, stress the role of peptization in the occurrence of spontaneous emulsification during the process.

** It may be supposed that with a very small excess of oil, an ultramicroscopic (colloidal) emulsion is formed with droplets of a size beyond the resolving power of the microscope.

SUMMARY

1. A study has been made of the degree of dispersion of spontaneously formed emulsions of solar oil, obtained with ammonium oleate, sodium naphthenic soap, sodium butylnaphthalene sulfonate (Nekal), and with mixtures of ammonium oleate with sodium butylnaphthalene sulfonate, and ammonium oleate with Petrov kontakt sodium soap.
2. The dispersion analysis data are correlated with the hydrophily (affinity for water) of the emulsifiers, a relative measure of which is taken to be the value of the surface activity at the aqueous solution - air boundary of separation.
3. From surface tension data, the emulsifiers investigated give the following hydrophily series: ammonium oleate < naphthenic soap < Petrov kontakt soap < sodium butylnaphthalene sulfonate.
4. It is established that naphthenic soap, as a substance of medium surface activity and hydrophily, is a more effective emulsifier than the strongly surface active and relatively oleophilic ammonium oleate and the weakly surface active hydrophilic Nekal.
5. It is established that a mixture of oleate and Nekal is superior to either one of these emulsifiers in emulsifying power. A mixture of oleate and Petrov kontakt soap emulsifies oil better than does oleate alone.
6. A possible explanation of the results is that a mixture is equivalent to a "balanced emulsifier" and in it the defects of hydrophobic and hydrophilic emulsifiers as emulsion stabilizers are mutually compensated. Naphthenic soap is a "balanced emulsifier", as is shown by its medium surface activity.
7. The use of a mixture of a hydrophobic and a hydrophilic emulsifier, or of an emulsifier with medium hydrophilic properties, evidently also favors maximum utilization of the oil in the emulsion in the form of a highly dispersed emulsified phase.
8. On the basis of the results obtained and of the views put forward concerning the role of emulsifiers in the spontaneous emulsification process and its relation to the molecular nature of emulsifiers, a conclusion is drawn as to the emulsifiers to be used for the production of a concentrated, highly dispersed, and stable emulsion, with minimum "loss" of oil in a solubilized form in the dispersion medium.

I express my gratitude to Academician P. A. Rebinder for his guidance in this work

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* See Consultants Bureau Translation, page 311.